

**Amendment**  
**U.S. Patent Application No. 09/851,536**

**REMARKS**

Claims 1, 2 and 4-8 are pending in the subject application. Claims 1, 2 and 4-7 stand rejected. New claim 8 has been added, and support for this new claim is provided throughout the specification. Favorable reconsideration of the application and allowance of all of the pending claims are respectfully requested in view of the following remarks.

Claims 1, 2, 4 and 7 stand rejected under 35 U.S.C. §103(a) as being obvious over UK Patent Application No. GB 2,214,382 to Howorth (“Howorth”) in view of U.S. Patent No. 6,254,806 to Valdna et al. (“Valdna”); and claims 5 and 6 stand rejected under 35 U.S.C. §103(a) as being obvious over Howorth in view of Valdna and further in view of U.S. Patent No. 5,541,012 to Ohwaki et al. (“Ohwaki”). Applicants respectfully traverse these rejections based upon the remarks as set forth below.

Initially, it is noted that a certified copy of the European application is being submitted with this Amendment to support Applicants’ claim for foreign priority. In addition, the Abstract has been amended in accordance with the Examiner’s requirement for corrections.

Regarding the rejection to the claims, the Examiner is respectfully requested to reconsider the rejection of independent claim 1 as being obvious over Howorth in view of Valdna. In response to the previous arguments made by Applicants, the final Office Action sets forth the Examiner’s position that Howorth describes an anti-stokes phosphor but does not disclose an anti-stokes phosphor that emits in the range of 950 nm to 1075 nm as recited in claim 1. In particular, the final Office Action sets forth the following statement by the Examiner (page 3, paragraph 6):

*“Valdna et al. was introduced to **expressly** provide a phosphor that emits in the range of 950 nm to 1075 nm regardless of the phosphor absorption range. At no point did the Examiner state, suggest, or imply that Valdna et al. provides an ‘anti-stokes phosphor’, as asserted by the Applicant.”* (emphasis in original)

By making this statement, the Examiner further supports Applicants’ position, as set forth in the previous Amendment filed October 4, 2004, that Valdna fails to make up for the noted

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deficiencies of Howorth, because Valdna fails to teach an anti-stokes phosphor that emits in the range of 950 nm to 1075 nm.

In essence, the Examiner's position is that Howorth teaches an anti-stokes phosphor, but not an anti-stokes phosphor that emits in the recited 950 nm to 1075 nm range. The Examiner then relies on Valdna for its teaching of a phosphor that emits within the recited range. However, as apparently acknowledged by the Examiner, the Valdna reference fails to teach an anti-stokes phosphor. Next, the Examiner asserts that it would have been obvious to provide a phosphor having the recited emission, as taught in Valdna, in the camera of Howorth. Even assuming this would be a reasonable modification of Howorth, at best this would suggest adding a phosphor that follows Stokes law and emits in the 950 nm to 1075 nm range, which fails to meet the limitation of an anti-stokes phosphor that emits in the recited range as recited in claim 1.

Alternatively, if the Examiner's position is that it would have been obvious to modify the anti-stokes phosphor of Howorth, based upon the teachings of Valdna, to emit in the recited 950 nm to 1075 nm range, this is clearly an improper and unreasonable combination of these references. There is no teaching in Valdna to indicate how or in what manner the phosphors of Howorth could be modified to emit within the recited range while still being anti-stokes phosphors.

As noted above, the Examiner states that Valdna is relied upon for its teaching of a phosphor that emits in the recited range *"regardless of the phosphor absorption range."* However, the phosphor absorption range cannot be disregarded, because that is an indication of whether the phosphor follows Stokes Law or is an anti-stokes phosphor. As noted in the specification of the application (page 1, lines 25-32) the term "anti-stokes" refers to an emission process that does not conform to Stoke's second law that a materials' fluorescence emission is lower in photon energy than the absorbed energy. In other words, an anti-stokes phosphor is capable of emitting at a wavelength that is smaller than its absorption wavelength. At best, Valdna teaches phosphors that are capable of receiving high energy x-rays and emitting lower energy photons in the visible or near-IR wavelength spectrum. Thus, Valdna teaches the use of

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phosphors that follow Stokes Law, which are not the same as an anti-stokes phosphor as recited in claim 1, regardless of whether the Valdna phosphors emit in the recited range of 950 nm to 1075.

In addition to the previous arguments, Applicants provide with this Amendment a copy of pages 643-647 taken from the textbook entitled "Phosphor Handbook." These pages provide additional information regarding characteristics of anti-stokes or up-conversion phosphors such as the type utilized in the claimed invention. These textbook pages further indicate the differences between anti-stokes phosphors and the phosphors taught in Valdna which follow Stokes Law.

The Examiner is therefore requested to reconsider and withdraw the rejection of claim 1 as being obvious over the combination of Howorth and Valdna.

Claims 2 and 4-7 depend from claim 1, and thus include all the limitations of this claim. Accordingly, these claims should also be allowed over any combination of Howorth and Valdna, and the Examiner is requested to reconsider and withdraw the rejection of these claims.

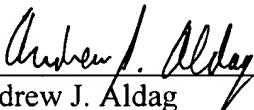
New claim 8 recites all of the features of claim 1, and further includes the feature that the anti-stokes phosphor is directly bound to the light receiving surface. Thus, in addition to the deficiencies of Howorth and Valdna as noted above with respect to the recited anti-stokes phosphor having the recited emission range, Howorth further fails to teach a phosphor that is directly bound to a light receiving surface as recited in claim 8. As noted by the Examiner, the phosphor 29 of Howorth is coupled to a light receiving surface by means of fiber optics 25. Thus, the phosphor 29 of Howorth is not directly bound to the light receiving surface as recited in claim 8. Accordingly, claim 8 should be allowed over Howorth in combination with Valdna and/or any of the other cited references.

In view of the foregoing, the Examiner is respectfully requested to find the application to be in condition for allowance with claims 1, 2 and 4-8. However, if for any reason the Examiner feels that the application is not now in condition for allowance, the Examiner is respectfully requested to call the undersigned attorney to discuss any unresolved issues and to expedite the disposition of the application.

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Applicant hereby petitions for any extension of time that may be required to maintain the pendency of this case, and any required fee for such extension is to be charged to Deposit Account No. 05-0460.

Respectfully submitted,

  
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## chapter twelve — section one

### Other phosphors

Yoh Mita

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#### 12.1 Infrared up-conversion phosphors

##### 12.1.1 Introduction

In this section, characteristic features of infrared-to-visible up-conversion phosphors doped with trivalent rare-earth ions are described. Devices made with these materials and important applications of such materials and devices are also mentioned. It is widely known that certain kinds of trivalent rare-earth-activated phosphors emit intense visible luminescence under near-infrared light excitation. This up-conversion process takes place in the following way: higher lying excited states of a rare-earth ion are populated by two- or three-step successive excitations with infrared quanta or by energy transfers. A downward transition to the ground level or to an intermediate excited level produces the visible luminescence. The up-conversion efficiency is known to be strongly dependent upon choice of host materials, activator and sensitizer concentrations, etc. However, since elementary processes governing the up-conversion processes are physically simple in nature and well explored, it seems now possible to review the entire up-conversion phenomenon in a consistent manner.

Infrared stimulation of visible luminescence is an anti-Stokes emission process (see Chapter 7). This phenomenon is due to the liberation by infrared excitation of carriers stored in traps and is produced by a different mechanism. However, these two phenomena are used in the same application, i.e., the detection of infrared laser light.

##### 12.1.2 Brief review up to the present

Generation of visible luminescence in rare-earth ion-doped materials as a result of successive photon absorption in excited levels was proposed in 1959 and has been termed

"quantum counter action."<sup>1</sup> Today, the same effect is generally called excited-state absorption (ESA) in contrast with ground-state absorption (GSA). The effect is observed particularly at high excitation densities such as those produced by high-power laser light excitation or those encountered in single-mode optical fibers.

Substantial improvement in the up-conversion efficiencies was realized by incorporating the  $\text{Yb}^{3+}$  ion as a sensitizer and by exploiting energy transfers between rare-earth ions.<sup>2</sup> This scheme is often called energy transfer up-conversion (ETU) or addition of photons by transfer of energy (APTE). Since  $\text{Yb}^{3+}$  ions have a substantially larger optical cross-section and a lesser tendency for concentration quenching in comparison with other rare-earth ions, higher excitation densities can be realized. The absorbed energy can then be efficiently transferred to such ions as  $\text{Er}^{3+}$  or  $\text{Tm}^{3+}$ , giving rise to green and red or blue emission, respectively.<sup>3,4</sup>

The effect of  $\text{Yb}^{3+}$  sensitization was first reported in  $\text{NaWO}_4$  microcrystals and approximately 50x improvement in up-conversion efficiency was observed.<sup>2</sup> Shortly thereafter, fluorides such as  $\text{LaF}_3$  and  $\text{YF}_3$  proved more suitable as host materials for rare-earth ion doping.<sup>5</sup> It was then found that the absorption band of  $\text{Yb}^{3+}$  ions provides a good match to the emission band of common GaAs:Si light-emitting diodes (LEDs) centering at 950 nm.<sup>6</sup> Extensive investigations have been carried out with the purpose of obtaining practical green-emitting LEDs by combining infrared-emitting LEDs with  $\text{Er}^{3+}$ - and  $\text{Yb}^{3+}$ -doped fluoride phosphors.<sup>7-9</sup> However, it soon became clear that these devices cannot compete with the more efficient green-emitting GaP LEDs, and interest for the systems has faded out.

Presently, the most important application of infrared up-conversion materials seems to be the detection of infrared light from laser diodes.<sup>10,11</sup> Since the visible emissions generated from these materials are quadratically or cubically dependent upon excitation intensity, detection is particularly favorable for intense or focused laser light.

In recent years, renewed interest has been directed toward up-conversion devices and materials. The interest is principally due to prospects for the realization of infrared up-conversion lasers pumped with laser diodes. The revival of interest for the up-conversion phenomenon is due to the advent of powerful and less costly 980-nm or 800-nm laser diodes that can be used as excitation sources and the appearance of new materials such as fluoride glass that can be manufactured in fiber form. The first report on an infrared up-conversion laser dates back to 1972, in which a  $\text{BaY}_2\text{F}_8$  crystal doped with  $\text{Ho}^{3+}$  and  $\text{Yb}^{3+}$  was used and green laser oscillations were observed at liquid nitrogen temperature.<sup>12</sup> More recently, up-conversion lasers oscillating in the green or blue spectral regions have been reported in long fibers<sup>13,14</sup> or in materials under excitation with high-power lasers.<sup>15,16</sup>

### 12.1.3 Mechanism and the materials for up-conversion of luminescence

Several typical up-conversion schemes are illustrated in Figures 1(a) to (e). The energy levels of trivalent rare-earth ions are discussed elsewhere (see 3.3). The simplest way for realizing up-converted emission is to induce successive absorption in a single ion. This scheme, called ESA, is illustrated in Figure 1(a) for the  $\text{Er}^{3+}$  ion.

Efficient up-conversion emission is observed in fluoride phosphors doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions. In these phosphors, the green emission at 550 nm is generated as a result of two successive resonant energy transfers from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  ions, followed by nonradiative decay to the green-emitting level,  $^4\text{S}_{3/2}$ , as is depicted in Figure 1(b). A typical emission spectrum is shown in Figure 2(a) for  $\text{YF}_3:\text{Yb}^{3+},\text{Er}^{3+}$  phosphors pumped by a 980-nm emitting laser diode. In some  $\text{Er}^{3+}$ -doped phosphors, red emission from  $^4\text{F}_{9/2}$  level predominates over the green emission. This is especially the case for phosphors such as

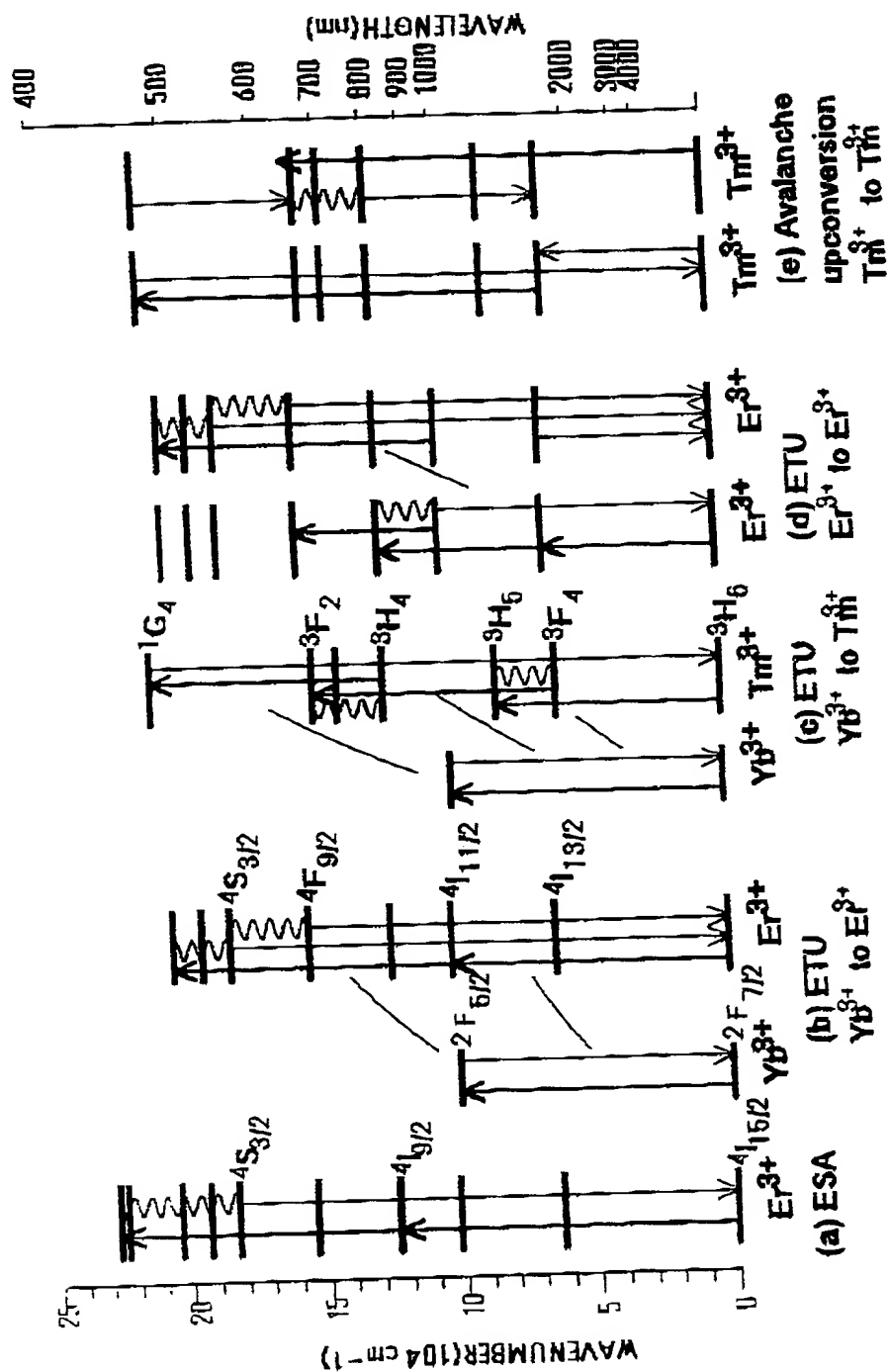


Figure 1 Schematic illustrations of various up-conversion processes: (a) excited state absorption (ESA); (b) infrared up-conversion with two resonant energy transfers ( $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$ ); (c) same with three phonon-assisted energy transfers ( $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$ ); (d) same with a more complicated energy transfer scheme in  $1.5\text{-}\mu\text{m}$  light detection ( $\text{Er}^{3+}$  to  $\text{Er}^{3+}$ ); (e) avalanche up-conversion ( $\text{Tm}^{3+}$  to  $\text{Tm}^{3+}$ )

the oxyhalides, which have larger phonon cut-off energies as compared to fluoride materials. Several possible excitation routes have been postulated for the red emission. All of these routes require multiphonon nonradiative decay to bridge large energy gaps or energy transfer steps assisted by the simultaneous emission of phonons to surmount the energy mismatch between two transitions.

Three successive phonon-assisted energy transfer steps from  $\text{Yb}^{3+}$  ions are required for generating the blue emission of  $\text{Tm}^{3+}$  ions, as shown in Figure 1(c). The blue emission from the  $^1\text{G}_4$  level is accompanied by red emission, which arises from an intermediate transition terminating at the  $^3\text{F}_4$  level. A typical emission spectrum for  $\text{YF}_3:\text{Yb}^{3+},\text{Tm}^{3+}$  phosphors is given in Figure 2(b).

There are several rare-earth ions, other than  $\text{Yb}^{3+}$ , that have relatively long excited-state lifetimes. The wavelengths can be extended from 1.0  $\mu\text{m}$  to the 0.8- $\mu\text{m}$  and 1.5- $\mu\text{m}$  regions by using these ions. In Figure 1(d), a typical excitation route for generating visible emissions when using 1.5- $\mu\text{m}$  excitation is depicted.

Recently, a new type of up-conversion luminescence, called avalanche up-conversion, has been reported in several  $\text{Tm}^{3+}$ -activated phosphors and has attracted considerable interest.<sup>17,18</sup> The mechanism of avalanche up-conversion is schematically shown in Figure 1(e). In this up-conversion scheme, the principal excitation takes place due to weak ground-state absorption combined with intense excited-state absorption. The up-conversion luminescence is weak under weak pump power. However, with increasing excitation power, the lower excited state becomes populated due to cross-relaxation between neighboring ions. This up-conversion luminescence is characterized by a threshold in the excitation power, above which a conspicuous increase of visible emission is observed. This up-conversion process is known to take place particularly at low temperatures and under high excitation intensity.

The following discussion on the up-conversion mechanism principally concerns ETU phenomena using  $\text{Yb}^{3+}$  as the sensitizer. Since the physical nature of the elementary processes involved in the up-conversion processes is well understood, the apparently complicated characteristics of ETU can be explained with relatively simple models in a straightforward manner. The elementary processes involved in the up-conversion phenomena include optical absorption both from ground (GSA) and excited states (ESA), radiative and nonradiative decay, and energy transfer. Energy transfer processes include those between different species of ions as well as those between the same kind of ions (known as energy migration or energy diffusion), and phonon-assisted transfers as well as resonant transfers. The nonradiative multiphonon decay rate is governed by the number of phonons needed to relax to the next lower level. It is known that the relaxation rate decreases approximately exponentially with the energy gap to the next lower level; in other words, with the number of emitted phonons.<sup>19,20</sup> The rate for the phonon-assisted energy transfer is also expected to be exponentially dependent upon the energy mismatch.<sup>21</sup>

Many important characteristics of up-conversion materials and devices can then be analyzed with a set of simple rate equations, taking various elementary processes into consideration. Results of such calculations and comparisons with experimental results are found in a number of publications.<sup>2,9,22</sup> However, it has also been shown that the simple rate equation model has limitations in some instances. Several important features are briefly reviewed in this article.

In many applications, fluoride materials such as  $\text{YF}_3$  or  $\text{BaY}_2\text{F}_8$  are considered to be advantageous. However, it has been shown recently that chlorides such as  $\text{BaCl}_2$  are more suitable as hosts for  $\text{Er}^{3+}$  ions than the fluorides.<sup>23</sup> This is due to a lower phonon cut-off frequency in the chlorides than in the fluorides. The smaller phonon energy brings about slower multiphonon decay rates; in other words, longer lifetimes of the excited levels



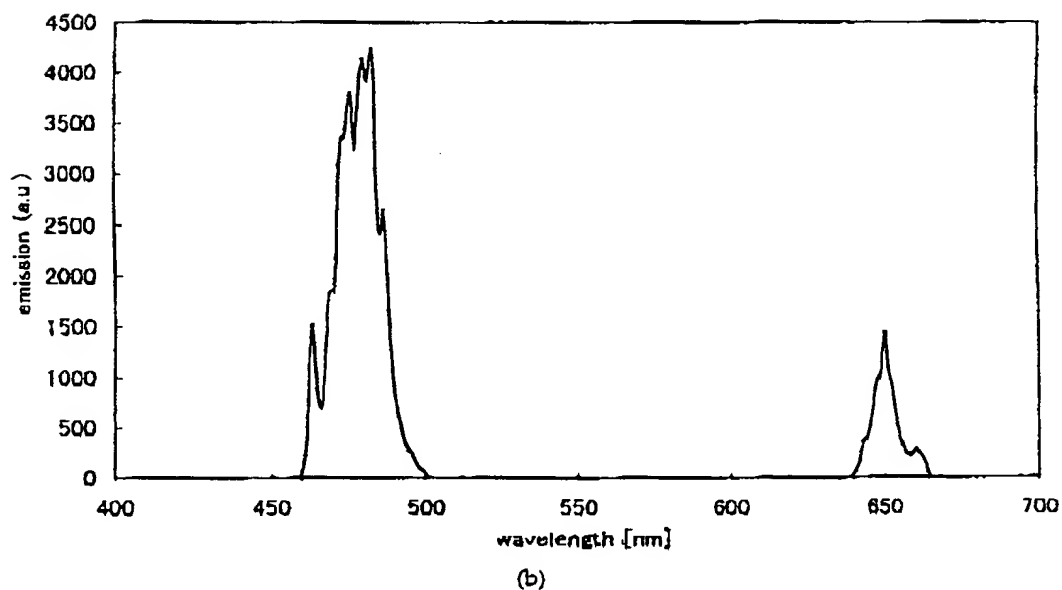
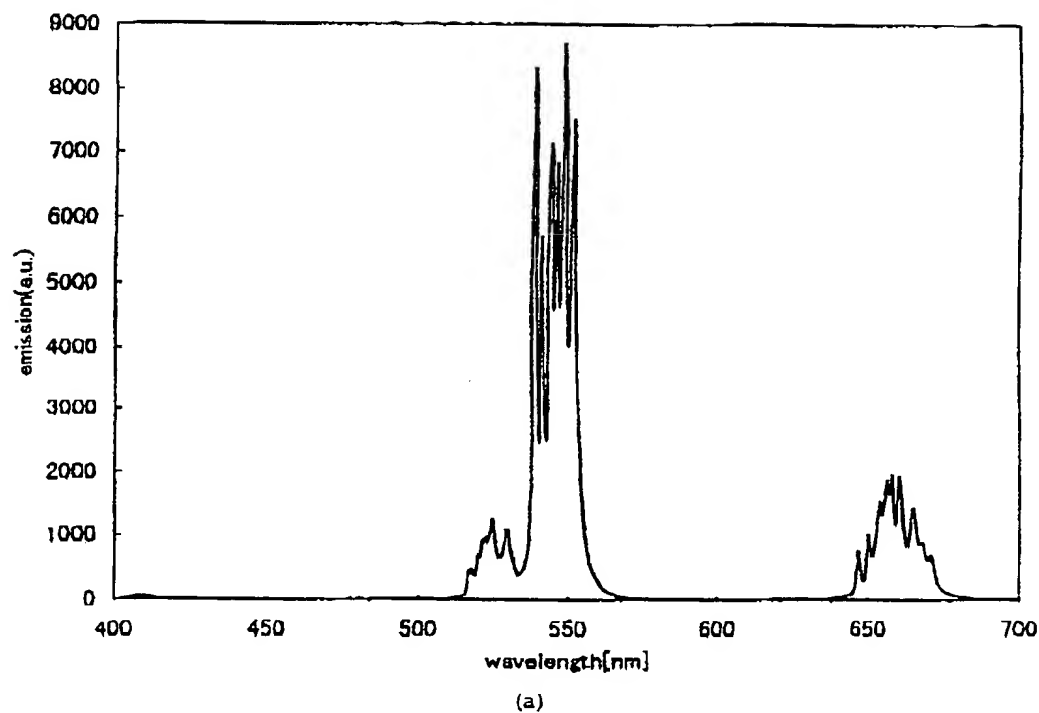


Figure 2 Typical up-conversion emission spectra under 980-nm light excitation in fluoride phosphors doped with  $\text{Yb}^{3+}$  as sensitizer: (a)  $\text{Y}_{0.78}\text{Yb}_{0.20}\text{Er}_{0.02}\text{F}_3$ ; (b)  $\text{Y}_{0.8}\text{Yb}_{0.2}\text{Tm}_{0.001}\text{F}_3$ . (Observed by the author.)

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